Hydrogen Cyanide Formation in the Gas-phase Radiolysis of Mixtures of Nitrogen and Ethylene

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Recently, several studies have been reported on the radiolytic isotopic exchange of nitrogen, in which the G-values of nitrogen atoms have been estimated to range from 9 to 19.[1-3] These values prompted us to investigate the radiolysis of gaseous mixtures of nitrogen and ethylene in an attempt to study the reactions of nitrogen atoms with ethylene molecules.

Experimental

Gaseous mixtures of nitrogen and ethylene in various pressures and ratios were irradiated with ^{60}Co γ-rays in sealed, 80-m*l* vessels made of Pyrex glass.

The nitrogen was purchased from the Takachiho Shoji Co. and was used without further purification. Gas chromatographic analysis showed that it contained 0.01% oxygen.

The dose rate was 1.25×10^6 R/hr; it was measured with a Fricke dosimeter, assuming that $G(\mathrm{Fe}^{3+})=15.5$.

Products were analyzed by gas chromatography; for hydrocarbons, use was made of a column packed with silica gel, and for hydrogen cyanide, a column of dioctyl phthalate.

Results

The major products observed are shown in Fig. 1 as a function of the nitrogen pressure.

Since hydrogen cyanide was the only observed product containing nitrogen atoms, the G-values were measured under a variety of conditions.

1. Table 1 shows the irradiation-time dependence of G(HCN).[*1]

TABLE 1. IRRADIATION TIME DEPENDENCE OF HYDROGEN CYANIDE FORMATION

$P(\mathrm{N_2})=564$ Torr, $P(\mathrm{C_2H_4})=6$ Torr

Irrad. time, hr	HCN, μmol	G(HCN)
5	0.18	0.51
10	0.29	0.42
20	0.28	0.20
30	0.25	0.12

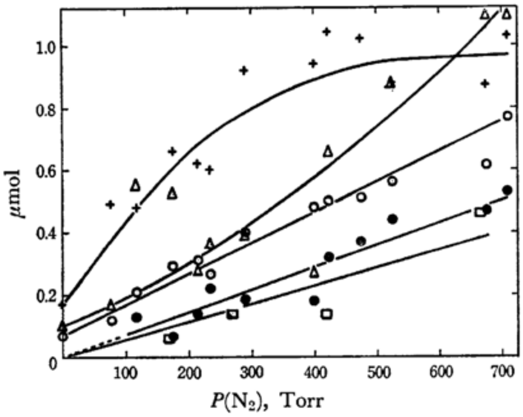

Fig. 1. Nitrogen pressure dependence of main product formation.
$P(\mathrm{C_2H_4})=33$ Torr, Irrad. time; 9 hr
+ Acetylene △ n-Butane
○ Ethane ● Propane
□ Hydrogen cyanide

2. The pressure change of nitrogen from 250 to 750 Torr did not vary the value (0.5) of G(HCN), where the pressure of ethylene was 6 Torr and the irradiation time was 5 hr.

3. When the ethylene pressure was varied from 6 to 34 Torr, while the pressure of nitrogen (550 Torr) and the irradiation time (10 hr) were kept constant, G(HCN) was again found to be constant (0.4).

4. In the presence of sulfur hexafluoride (1 to

[*1] Calculation of G(HCN) is based on the energy absorbed by the nitrogen.

1) M. Anbar and P. Perlstein, *J. Phys. Chem.*, **68**, 1234 (1964).

2) D. H. Dawes and R. A. Back, *ibid.*, **69**, 2385 (1965).

3) R. Shimozawa and K. Ooshima, Proceedings for the 10th Discussion Meeting of Radiation Chemistry, Hiroshima (October, 1967).

3 Torr), G(HCN) increased up to 0.8 from 0.4 (the latter value being obtained in the absence of sulfur hexafluoride), where the nitrogen was at 560 Torr, the ethylene was at 7 Torr, and the irradiation time was 10 hr.

5. When *trans*-2-butene (7 Torr) was used in place of ethylene, where the nitrogen was at 550 Torr and the irradiation time was 10 hr, practically no hydrogen cyanide formation was observed. When both ethylene (6 Torr) and *trans*-butene (7 Torr) were present, G(HCN) found was 0.1_7.

Discussion

Since G(HCN) does not vary with the change in the pressure of ethylene (result 3), it is obvious that hydrogen cyanide is formed by the reaction of active species from nitrogen with ethylene. By extrapolating the values in Table 1 to zero time, the initial G(HCN) value is estimated to be 0.8. The decrease in G(HCN) with the irradiation time may be due to the electron scavenging of the product, hydrogen cyanide,4) followed by decomposition. The value of 0.8 is in agreement with that obtained in the presence of sulfur hexafluoride (result 4). Consequently, the G-value of active species responsible for the formation of hydrogen cyanide may be estimated to be 0.8.

The independency of G(HCN) of the pressure of nitrogen suggests that the active species are not excited nitrogen molecules. If excited nitrogen molecules are responsible for the formation of hydrogen cyanide, a decrease in G(HCN) should be observed with an increase in the pressure of nitrogen because of the deactivation. Moreover, it is generally accepted, in the study of active nitrogen produced by electric discharge, that the species responsible for the formation of hydrogen cyanide are nitrogen atoms, but not excited molecules.5) Therefore, we can safely say that the active species leading to the formation of hydrogen cyanide in the present system are nitrogen atoms and/or nitrogen atom ions. The reaction may be as follows:

$$N\ (\text{or } N^+) + C_2H_4 \rightarrow HCN + CH_3\ (\text{or } CH_3^+)$$

The methyl radical or ion formed here probably reacts with ethylene and yields propane as the final product.

When *trans*-2-butene was used in place of ethylene, we could not detect the formation of hydrogen cyanide, but in the presence of both olefins we found a small amount of hydrogen cyanide (result 5). This suggests that *trans*-butene reacts with active species produced from nitrogen, but does not yield hydrogen cyanide. Therefore, we carried out a careful search for products containing nitrogen atoms, but could not find any. One possibility is the interference of some impurity in *trans*-butene, although none could be detected.

Nitrogen atoms may be considered to be formed as follows:

$$N_2-\begin{cases} \rightsquigarrow N_2^+ + e & (1) \\ \rightsquigarrow N + N^+ + e\ (\text{or } N + N) & (2) \end{cases}$$

$$N_2^+ + e \rightarrow 2N \qquad (3)$$

In the presence of ethylene, however, the reaction (3) competes with ion-molecule reactions, including the following reaction:

$$N_2^+ + C_2H_4 \rightarrow N_2 + C_2H_4^+ \qquad (4)$$

The ions produced may decompose immediately or may react with other ethylene molecules. The rate of the reaction (4) will be more than 10^{-10} cc molecule^{-1} sec^{-1}, judging from a similar reaction in rare gases,6) while the rate of the reaction (3) may be less than 10^{-6} cc molecule^{-1} sec^{-1}.7) Under the conditions of the present experiment (a few Torr of ethylene and a dose rate of about 10^6 R/hr), the contribution of the reaction (3) to the formation of nitrogen atoms may be negligibly small.

According to a recent report on the electron impact of nitrogen,8) a part of the ionization is dissociative. If we take 14% for the fraction of the dissociative ionization (this value corresponds to that obtained by the impact of 50 eV-electrons), the G-values of the nitrogen atoms and nitrogen atom ions estimated above can be interpreted well.

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4) M. Inoue, *J. Chim. Phys.*, **63**, 1061 (1966).

5) B. Brocklehurst and K. R. Jennings, "Progress in Reaction Kinetics," Vol. 4, ed. by G. Porter, Pergamon Press, Oxford (1967).

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7) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Clarendon Press, Oxford (1952), p. 631.

8) D. Rapp, P. Englander-Golden and D. D. Briglia, *J. Chem. Phys.*, **42**, 4081 (1965).